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AIR QUALITY MARATHON

Annual Report, 1979

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AIR QUALITY

MARATHON

Annual Report, 1979

TECHNICAL SUPPORT SECTION
NORTHWESTERN REGION
ONTARIO MINISTRY OF THE ENVIRONMENT

September, 1980

CONTENTS

SUMMARY

Air quality assessment investigations in Marathon have been conducted by the Ministry since 1974.

In 1979, vegetation near a local kraft pulp mill and in the townsite was free of injury symptoms caused by sulphur dioxide. No sulphur dioxide damage has been seen since 1976.

Mercury concentrations in snow and in moss experimentally exposed near the mill declined further from 1978 to 1979. Mercury in vegetation and in surface soil in the same area showed little change from 1978 to 1979, but was still well below levels reported for 1977, before a chlor-alkali plant adjacent to the pulp mill was closed. Mercury contamination persisted in soil in a small area near the mill's main effluent outfall into Lake Superior and near a company warehouse formerly used for temporary storage of mercury-laden waste. Concentrations of mercury in the air, vegetation, soil, and snow in the townsite were normal.

Excessive fallout of calcium was found near the lime kiln on the south side of the mill. Sodium deposition in the same area, however, was well below levels for the period preceding the commissioning of a new recovery furnace and tall stack.

Dustfall measurements in the townsite rarely exceeded Ontario regulations. Emissions of particulate matter from the mill had no significant impact on dustfall measured outside its immediate vicinity.

Average sulphation levels at the five Marathon monitoring stations declined sharply in March and succeeding months, following the start-up of the mill's new recovery furnace. Despite this improvement, it is suspected that provincial air quality objectives for sulphur dioxide and reduced sulphur may be exceeded from time to time. A proposed control order contains provisions which should result in full compliance with provincial regulations by late 1984.

INTRODUCTION

The Ministry of the Environment has conducted an air quality assessment programme at Marathon since 1974. These studies (1, 2, 3, 4) demonstrated that emissions from a local bleached kraft pulp mill and adjacent chlor-alkali plant resulted in elevated levels of mercury and particulate matter nearby. In the town area, approximately 500 to 1000 m (metres) to the east of the mill, mercury concentrations were normal, and fallout of particulate matter emitted by the mill was not considered significant. Levels of obnoxious odours were, however, above acceptable concentrations when winds carried mill emissions over the townsite.

Investigations in 1979 continued most aspects of the work carried out in earlier years, including vegetation and soil studies, snow sampling, and air quality monitoring.

VEGETATION AND SOIL ASSESSMENT

Vegetation in the vicinity of the pulp mill was examined in late June and late July. There was no evidence of visible sulphur dioxide injury on either occasion. Vegetation damage caused by this pollutant has not been recorded at Marathon since 1976. Minor insect injury, unrelated to mill operations, was noted on several kinds of trees and shrubs in July.

Triplicate samples of a local weed, cow parsnip (Heracleum lanatum), were obtained on July 31 from 11 sites near the mill (Figure 1) and at two control locations. Standard Ministry sampling and sample processing procedures (2) were followed. The collected material was submitted to the Ministry's Thunder Bay laboratory for calcium, mercury and sodium analysis and to the Toronto laboratory for chloride and sulphur determinations.

Chemical analysis results for the cow parsnip samples are presented in Table 1. Mercury showed little change in distribution pattern or concentration from 1978, but was well below the levels in 1976 (Table 2) before the mercury-cell chlor-alkali plant was closed. The calcium content of cow parsnip was extremely high near the pulp mill's lime kiln stack. In this area, a white powdery deposit, probably calcium oxide, was conspicuous on vegetation foliage. Although sodium was also elevated immediately south of the mill, the maximum concentration of 4000 µg/g (micrograms of sodium per gram of dried foliage) in 1979 was much lower than the value of 11000 µg/g in 1978. This improvement is attributed to a reduction in emissions from the new recovery furnace and better dispersion through use of a taller stack. For the same reasons, the sulphur content of cow parsnip also declined in 1979. Chloride showed some evidence of reduction, but the trend was less clear than that for sodium and sulphur.

SOIL

Surface soil, to a depth of 5 cm (centimetres), was collected by the normal method (3) from 10 sites (Figure 2) and from two controls. The analytical results for mercury, determined by the Ministry's Thunder Bay laboratory, are summarized in Table 3, which also includes comparable data for 1976 and 1978. The 1979 results show that mercury contamination persisted in surface soil on the south side of the mill, in a small area near the mill's main effluent discharge point into Lake Superior, and along the perimeter fence at the company's warehouse near a location formerly used for temporary storage of mercury-laden waste. There was some fluctuation in mercury concentrations between 1976, 1978 and 1979, but there was no obvious trend.

SNOW SAMPLING

Core samples of the total snow depth were obtained in March, 1979, from 11 sites in the study area (Figure 3a) and from two controls. Standard sampling and analytical procedures were employed. The snow meltwater was analyzed for mercury only, at the Ministry's Thunder Bay laboratory.

Mercury levels in snow (Table 4) decreased significantly from 1976 to 1979 and were above background in 1979 only in the immediate vicinity of the chlor-alkali plant (Figure 3b). Mercury near the warehouse (site 17) also declined to a level only slightly above background.

AIR QUALITY MONITORING

PARTICULATE MATTER

Moss Exposure Trial

Mosses are effective in absorbing and retaining certain kinds of air pollutants. During a 40-day period from June 21 to July 31, 1979, small samples of Sphagnum moss were set out at 10 sites around the kraft mill (Figure 2). Chloride and sulphur in the moss were analysed at the Ministry's Toronto laboratory, and calcium, mercury and sodium levels were determined at the Thunder Bay laboratory. Two exposed and two unexposed controls provided information on background contamination.

Mercury concentrations in moss in 1979 showed further decline from levels recorded in earlier years, as illustrated by the data in Tables 5 and 6. By 1979, only one value was significantly above background. Calcium was very high in moss exposed on the south side of the mill (Table 5). Concentrations as high as 40 percent calcium were recorded. White, powdery dust was found on several moss-bag brackets in the vicinity of the

lime kiln. The dust was about 70 percent calcium and was assumed to be calcium oxide. In contrast to calcium, sodium dropped sharply in 1979 (Table 5 and 6) following the start-up of the new recovery furnace and use of a new, taller stack. Chloride also showed some reduction from the levels reported for 1976. Sulphur concentrations, determined for the first time in 1979, revealed some elevated values close to the mill.

Dustfall

Dustfall was measured throughout the year at four of the sites shown in Figure 4. Standard Ministry practice was followed in sampling and analysis. Total dustfall and soluble sulphate were determined in the Thunder Bay laboratory.

In 1979, the monthly air quality objective for dustfall was nearly always met. The one high level, in June at station 63029, was attributed to road dust. Soluble sulphate was rarely above normal background and showed little variation from month to month. There was no relationship between dustfall levels and distance from the mill. Although there have been substantial fluctuations in average annual dustfall in Marathon over the past 5 years, the Ministry believes that these variations have been due to local influences near each monitoring site and not due to emissions from the mill.

SULPHATION RATE

Monthly sulphation rates provide a semi-quantitative estimate of average amounts of sulphur-containing gases in the atmosphere. The method is based on the conversion of lead dioxide to lead sulphate and will yield readings in the presence of any reactive compound, including sulphur dioxide and reduced sulphur. Despite its limitations, the sulphation method is useful in defining problem areas and in determining long-term trends.

The sulphation readings for 1979 are presented in Table 7. The table shows that values fell sharply in March and subsequent months, after the new recovery furnace came on stream. As a result of this improvement, averages for 1979 (Table 8) also declined relative to other years. Despite the evident benefits of the mill modernization and pollution control program, full compliance with provincial air quality objectives for sulphur dioxide and total reduced sulphur has not been confirmed. A proposed control order requires a report, by the end of 1980, on emissions of all airborne contaminants from the mill. Any source of emissions at the mill which fails to meet Ministry standards will be required to comply with Ontario regulations by late 1984.

MOBILE MONITORING SURVEY

Results from a survey conducted in Marathon in 1978 with mobile monitoring equipment have recently become available (5). During 35 hours of monitoring time on August 29, August 31, and September 1, 1978, the concentration of total reduced sulphur (TRS) exceeded the Ontario guideline (27 parts per billion, 30-minute average) for over 8 hours, or approximately 25 percent of the time. The maximum half-hour average was 73 ppb, recorded at the water tower in the centre of the townsite. Readings above the guideline were found as far as Highway #17, 5 to 7 kilometres from the mill. Analysis by gas chromatography showed that approximately 41 percent of the TRS was hydrogen sulphide, 36 percent was ethyl mercaptan, and 23 percent was methyl mercaptan. Sulphur dioxide and nitrogen oxide concentrations were low.

The mobile survey was undertaken when the tall stack was in use for discharging power boiler emissions, but before the new recovery furnace was operating. Consequently, sulphur dioxide and nitrogen oxide levels were acceptable, but TRS concentrations were undesirably high. This information is now of historical interest only: the installation of the recovery furnace has led to significant improvements, as noted earlier.

REFERENCES

1. Griffin, H. D. 1976. Air quality, Marathon. Annual Report, 1975. Ontario Ministry of the Environment.

2. Ontario Ministry of the Environment. 1977. Air quality, Marathon. Annual Report, 1976.

3. Ontario Ministry of the Environment. 1978. Air quality, Marathon. Annual Report, 1977.

4. Ontario Ministry of the Environment. 1979. Air quality, Marathon. Annual Report, 1978.

5. Ontario Ministry of the Environment. 1980. Ambient air survey in the areas of Thunder Bay, Red Rock, Marathon and Terrace Bay - 1978. ARB-TDA Report No. 47-80.

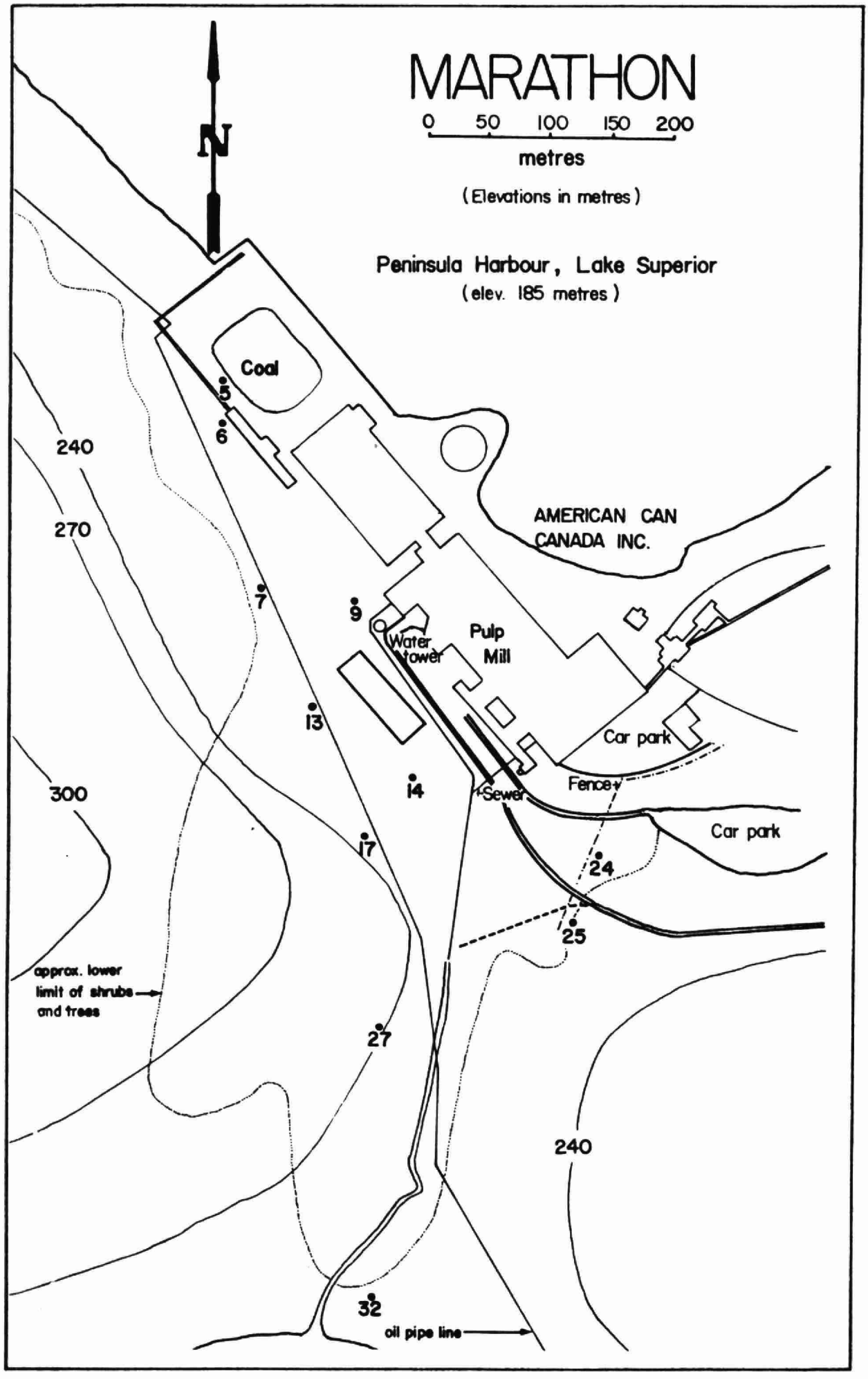

Figure 1. Cow parsnip sampling sites, 1979.

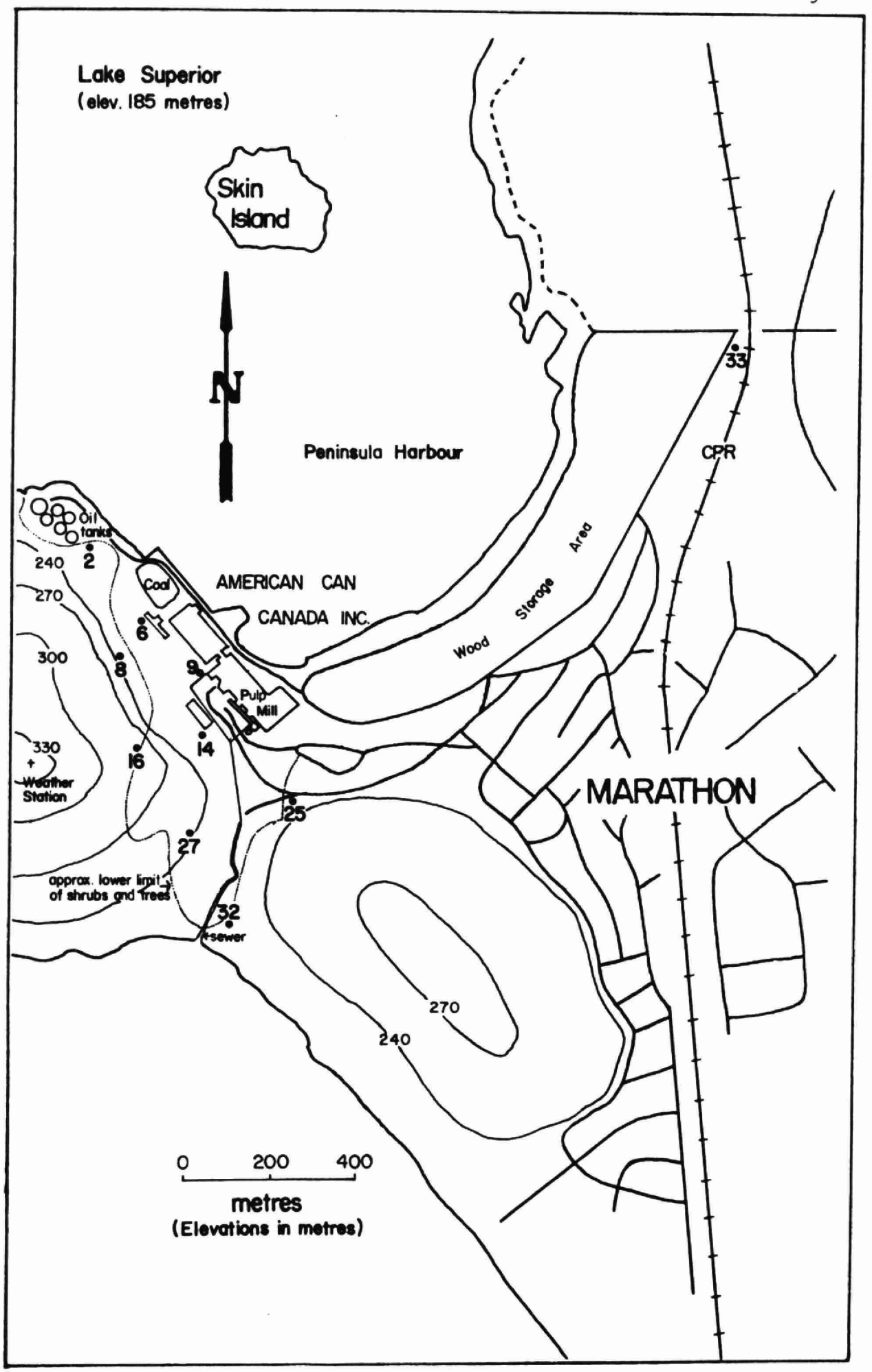

Figure 2. Soil sampling and moss exposure sites, 1979.

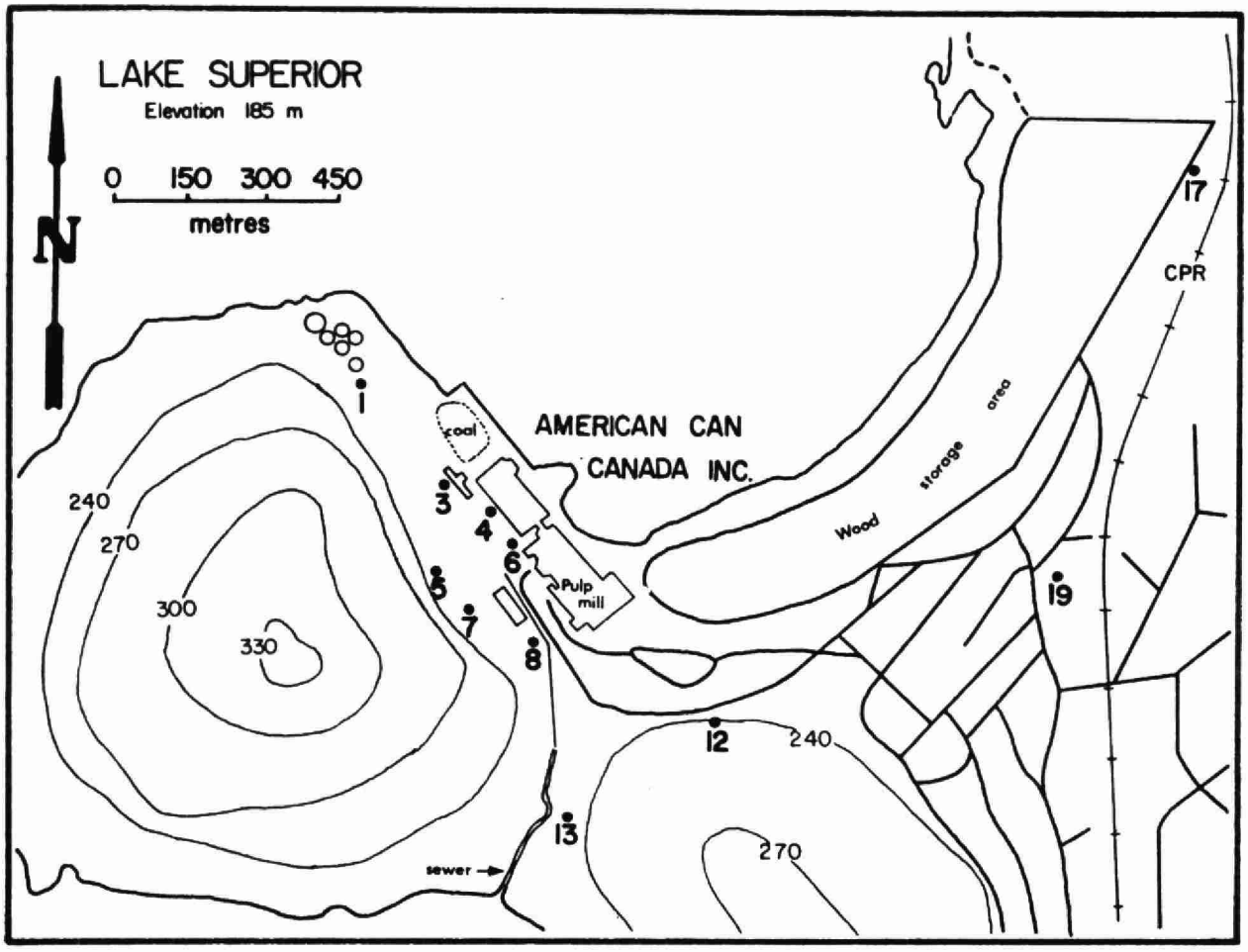

Figure 3a. Snow sampling sites, March, 1979.

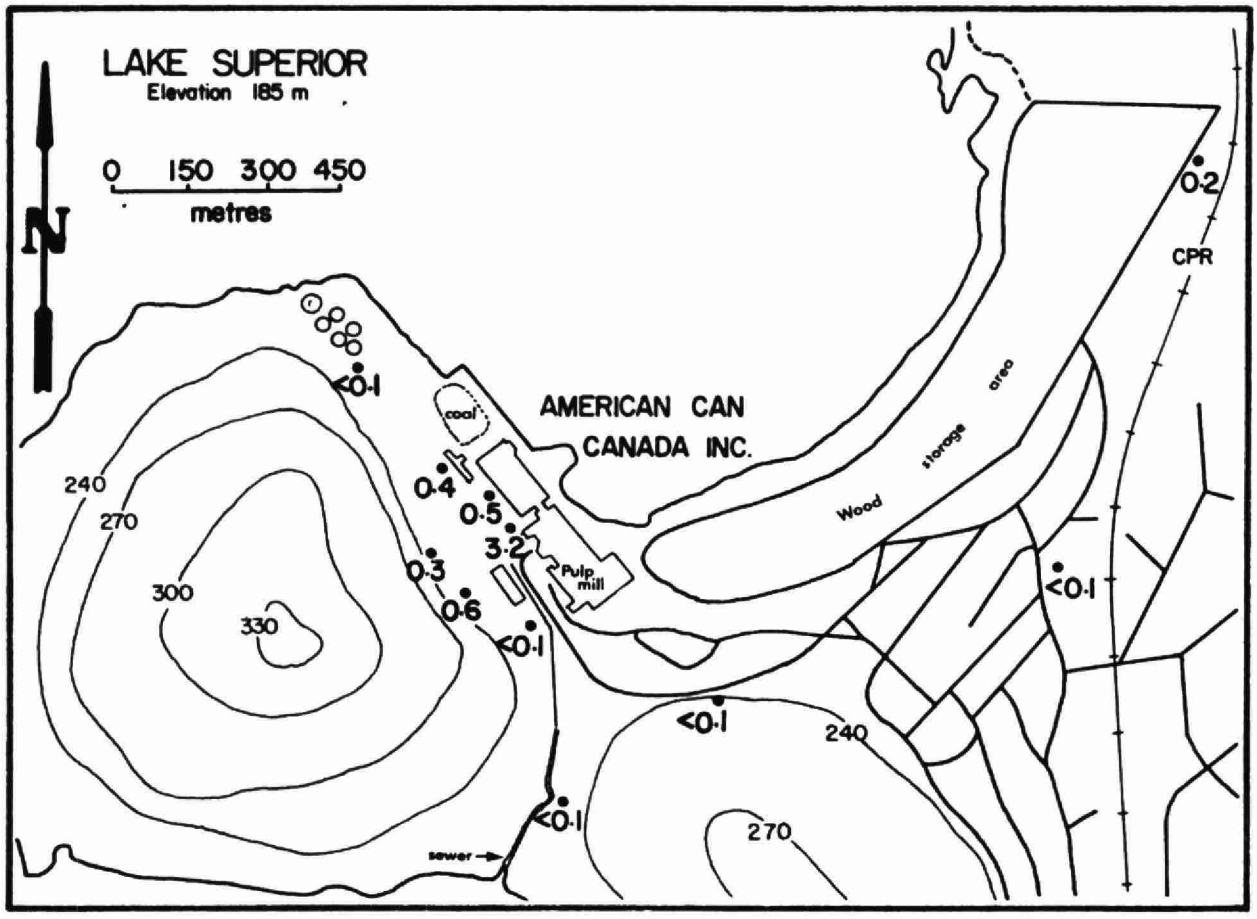

Figure 3b. Mercury levels (µg/l) in snow, March, 1979.

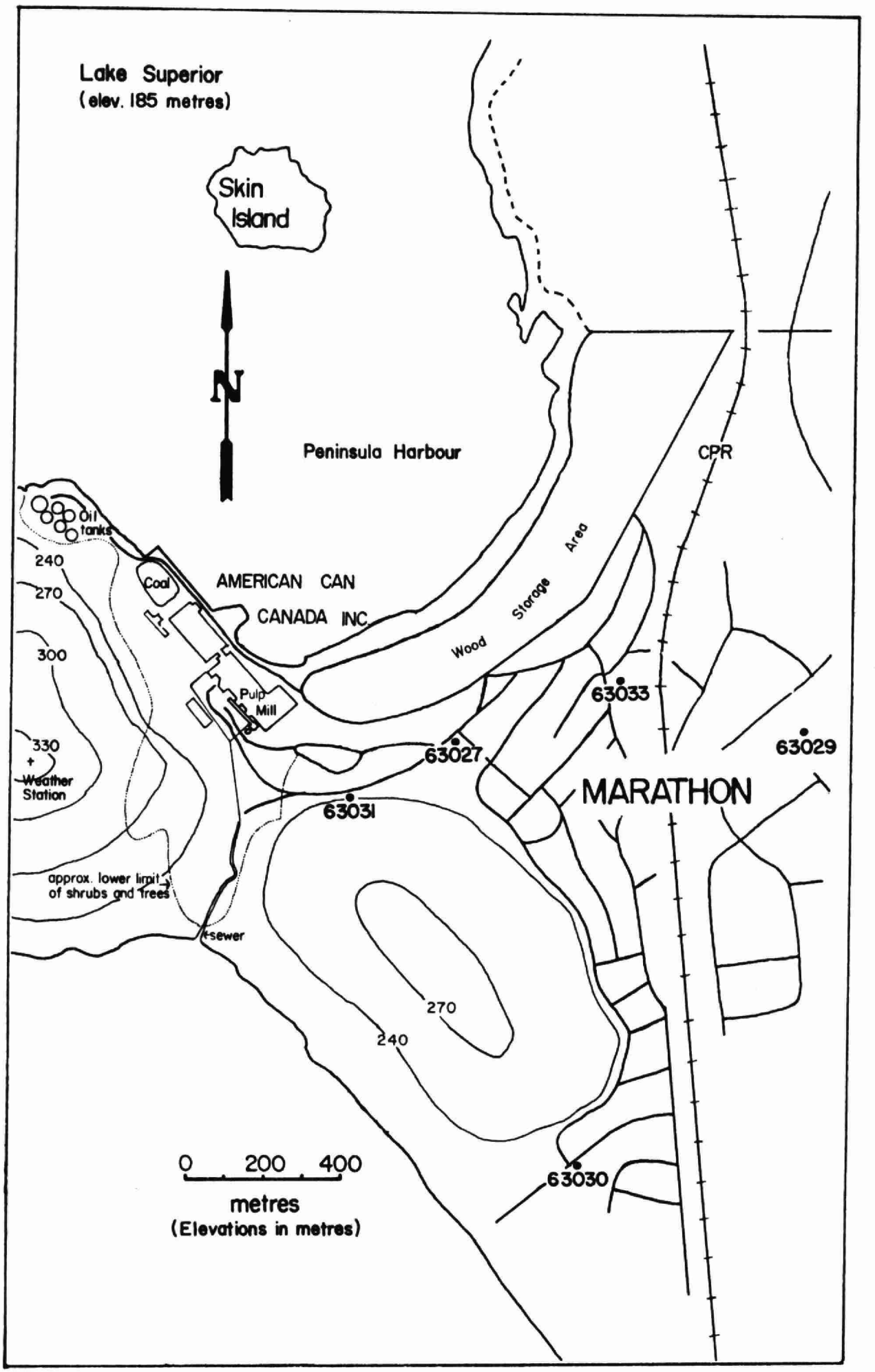

Figure 4. Air quality monitoring sites, 1979 (except station 63032, Heron Bay).

TABLE 1. Concentrations (dry weight basis) of calcium, chloride, mercury, sodium and sulphur in unwashed foliage of cow parsnip sampled July 31, 1979.

Sampling site (Figure 1)	Calcium %	Chloride %	Mercury µg/g	Sodium µg/g	Sulphur %
5	5.5	1.5	0.2	420	0.3
6	7.2	1.0	0.2	710	0.4
7	6.0	0.8	0.2	530	0.3
9	5.7	0.8	0.9	540	0.5
13	6.4	0.8	0.5	520	0.4
14	48.0	0.8	<0.1	4000	0.6
17	14.0	1.0	0.2	1500	0.4
24	6.9	0.8	<0.1	350	0.3
25	9.8	1.0	<0.1	1400	0.4
27	16.0	0.7	<0.1	2400	0.5
32	8.5	1.1	<0.1	690	0.4
controls	3.4	0.2	<0.1	38	0.2
normal background			<0.1	<600	

TABLE 2. Comparison between mercury in unwashed cow parsnip foliage collected in 1976, 1978 and 1979.

Sampling site (Figure 1)[a]	Mercury concentrations (µg/g, dry weight) 1976	1978	1979
6	1.3	0.2	0.2
7	2.1	0.2	0.2
9	26.0	0.8	0.9
17	2.0	0.1	0.2
24	7.6	<0.1	<0.1
27	0.9	<0.1	<0.1
controls	<0.1	<0.1	<0.1

[a]some locations differed slightly in 1976, 1978 and 1979

TABLE 3. Mercury levels (µg/g, dry weight basis) in surface soil (0-5 cm) sampled in 1976, 1978 and 1979.

Sampling site (Figure 2)[a]	1976	1978	1979
2	3.6	5.0	2.2
6	14.0	18.0	18.0
8	3.1	5.4	4.5
9	36.0	58.0	40.0
14	18.0	12.0	2.7
16	2.9	3.3	2.6
25	1.5	1.5	0.8
27	1.4	1.3	3.7
32	48.0	43.0	32.0
33	12.0	7.0	8.2
controls	<0.1	0.1	<0.1
normal background	<0.3	<0.3	<0.3

[a]some locations differed slightly in 1976 and 1978

TABLE 4. Comparison between average mercury levels (µg/l) in meltwater from snow sampled in Marathon in 1976, 1978 and 1979.

Sampling site (Figure 3a)	1976	1978	1979
1	0.4	0.5	<0.1
3	4.4	0.9	0.4
4	41.0	4.3	0.5
5	3.7	1.4	0.3
6	83.0	26.0	3.2
7	8.1	2.0	0.6
8	9.3	1.6	<0.1
12	<0.1	--	<0.1
13	0.6	0.3	<0.1
17	3.3	1.8	0.2
19	<0.1	<0.1	<0.1
controls	<0.1	<0.1	<0.1

TABLE 5. Concentrations of calcium, chloride, mercury, sodium and sulphur in *Sphagnum* moss exposed from June 21 to July 31, 1979.

Sampling sites (Figure 2)	Calcium %	Chloride µg/g	Mercury µg/g	Sodium µg/g	Sulphur µg/g
2	1.4	<100	0.2	250	50
6	1.4	<100	0.4	200	70
8	1.3	<100	0.2	110	60
9	2.3	700	2.7	260	110
14	40.0	300	0.1	2700	390
16	1.0	400	0.2	310	80
25	11.0	500	0.1	680	250
27	7.7	300	0.2	960	160
32	3.0	1200	0.2	210	90
33	1.3	<100	0.2	150	60
Exposed controls	1.0	200	0.2	240	60
Unexposed controls	0.5	200	0.1	220	55

TABLE 6. Comparison between mercury and sodium (both in µg/g, dry weight basis) in *Sphagnum* moss exposed for designated periods in 1976, 1977, 1978 and 1979.

Sampling sites (Figure 2)[a]	Mercury				Sodium			
	Year and exposure period (days)				Year and exposure period (days)			
	1976 (30[a])	1977 (51)	1978 (36)	1979 (40)	1976 (30[a])	1977 (51)	1978 (36)	1979 (40)
2	0.6	1.0		0.2	<1000	1800		250
6	2.4	3.5	0.4	0.4	2000	3500	22000	200
8	1.1	0.8	0.1	0.2	1000	1900	690	110
9	48.0	180.0	5.4	2.7	4000	2500	24000	260
14	6.8	8.9	0.5	0.1	28000	8900	12000	2700
16	0.6	0.2	0.4	0.2	5000	450	610	310
25	0.2	0.5	0.1	0.1	1000	690	8300	680
27			0.2	0.2			11000	960
32	0.2	0.3	0.1	0.2	<1000	1000	6100	210
33				0.2				150
exposed controls	<0.1	<0.1	0.1	0.2	<1000	110	180	240
unexposed controls		<0.1	0.1	0.1		70	62	220

[a]some locations differed slightly from year to year

TABLE 7. Dustfall and sulphation rates, Marathon, 1979.

Station	Location	Distance (metres) and direction from source[a]	Jan	Feb	Mar	Apr	May	Jun	Jul	Aug	Sep	Oct	Nov	Dec	Mean
			Dustfall (g/m^2/30 days)												
63027	McLeod/Abrams	640 ESE	4.4	1.3	6.7	5.1	5.5	7.0	7.7[b]	6.1	7.3	4.5	4.4	1.9	5.2
63029	Marathon Shell	1440 E	2.2	0.9	3.4	4.3	-	12.6	4.8	6.4	7.1	2.4	3.2	1.1	4.4
63030	Howe/Yawkey	1440 SE	1.7	0.5	3.0	4.0	4.5	3.9	1.9	2.9	2.6	1.0	1.9	0.8	2.4
63033	Water Tower	1010 E	1.4	0.1	2.4	3.8	5.0	4.5	6.3	3.4	3.5	1.9	2.0	0.4	2.9
			Sulphation rates (mg SO_3/100 cm^2/day)												
63027	McLeod/Abrams	640 ESE	.36	.45	.09	.03	.11	.05	.07	.12	.08	.10	.15	.20	.15
63029	Marathon Shell	1440 E	.21	.31	.11	.03	.11	.10	.06	.07	.06	-	.27	.50	.17
63030	Howe/Yawkey	1440 SE	.24	.64	.15	.06	.08	.09	.04	.04	.05	.08	.11	.27	.15
63031	Bark Press Road	450 SE	.52	.61	.10	.07	.08	.06	.11	.11	.11	.20	.16	.18	.19
63032	Heron Bay	14000 SE	.10	.25	.08	.03	.07	.12	-	-	.08	.08	.03	.19	.10
63033	Water Tower	1010 E	.23	.47	.16	.03	.14	.12	.16	.10	.11	.08	.04	.28	.16

[b] Values exceeding maximum acceptable levels of 7.0 (monthly) or 4.6 (annual average) are underlined.

[a] source arbitrarily designated as recovery furnace and power boiler stack, American Can Canada Inc. kraft pulp mill

TABLE 8. Comparison between average annual sulphation rates (mg SO_3/100 cm^2/day) from 1976 to 1979.

Station	1976	1977	1978	1979
63027	.22	.27	.37	.15
63028	.14	.17		
63029	.15	.17	.20	.17
63030	.18	.23	.23	.15
63031	.46	.56	.71	.19
63032			.10	.10
63033				.16

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